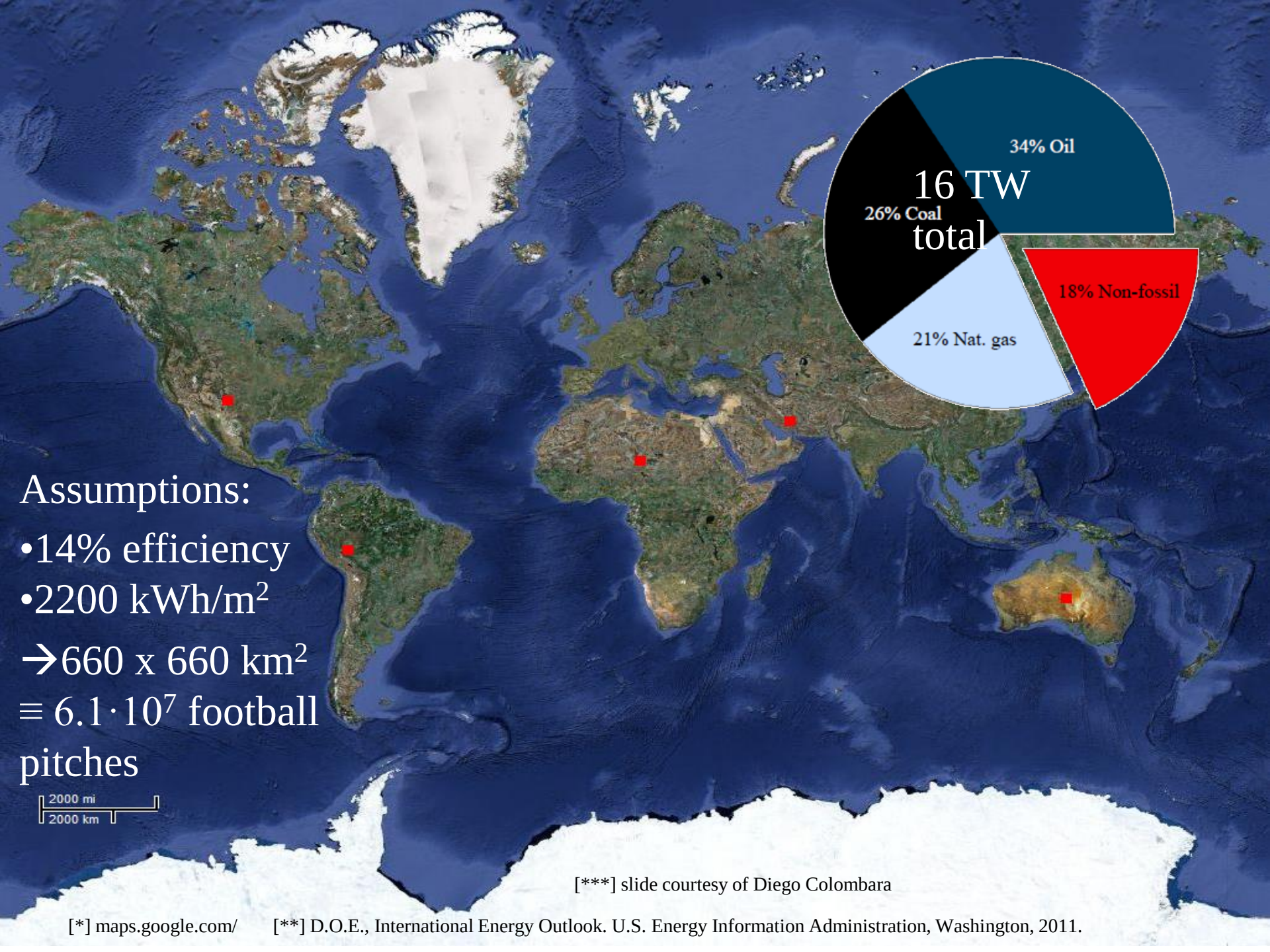
Kesterite, $Cu_2ZnSn(S,Se)_4$, for earth abundant photovoltaics: can we make single phase thin films, and does it matter?

- Why earth abundant photovoltaics?
- Some properties of kesterites
- Synthesis methods
- The voltage challenge
- How to overcome the V_{oc} challenge?

Phillip Dale
Laboratory for Energy Materials
University of Luxembourg



Assumptions:

- 14% efficiency
- 2200 kWh/m^2

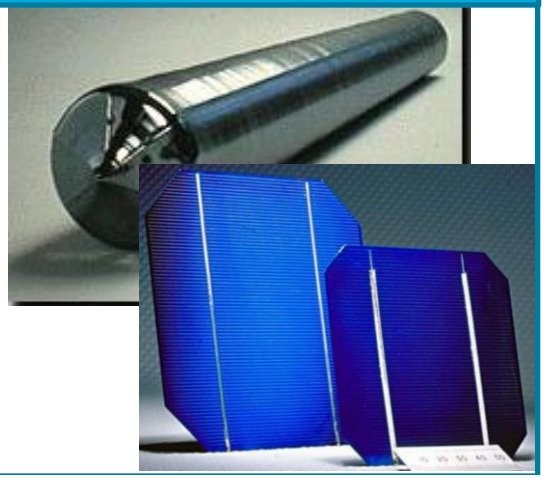
→660 x 660 km^2 ≡ 6.1·10^7 football pitches

[***] slide courtesy of Diego Colombara

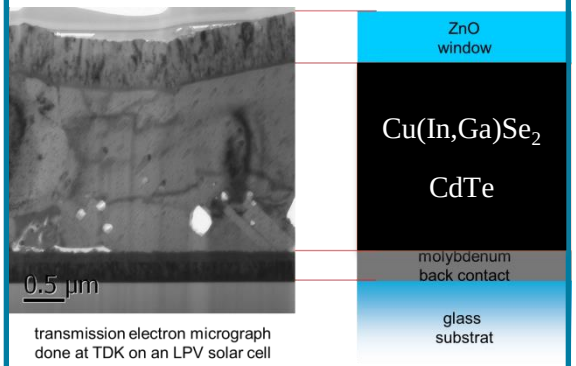
[*] maps.google.com/ [**] D.O.E., International Energy Outlook. U.S. Energy Information Administration, Washington, 2011.

Photovoltaic technologies

Silicon – 26 %



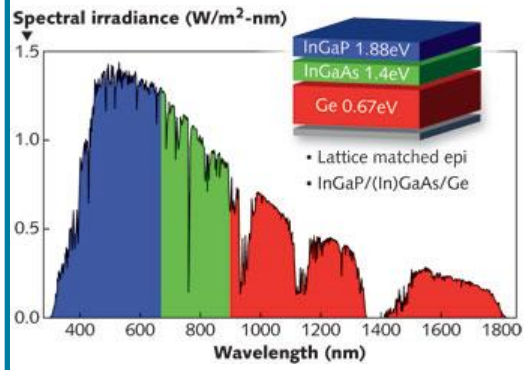
Inorganic – 22 %



transmission electron micrograph
done at TDK on an LPV solar cell

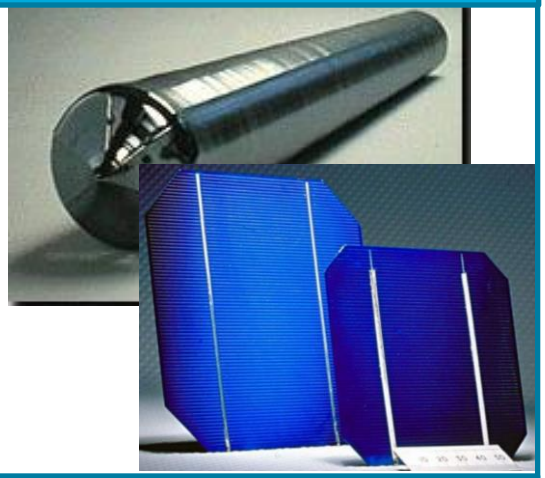
III - V– 38 %

www.laserfocusworld.com

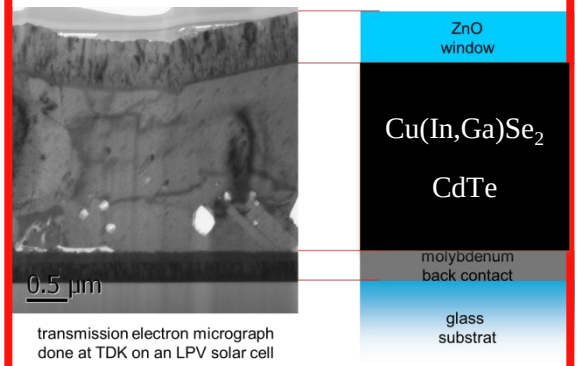


Photovoltaic technologies

Silicon – 26 %



Inorganic – 22 %



transmission electron micrograph
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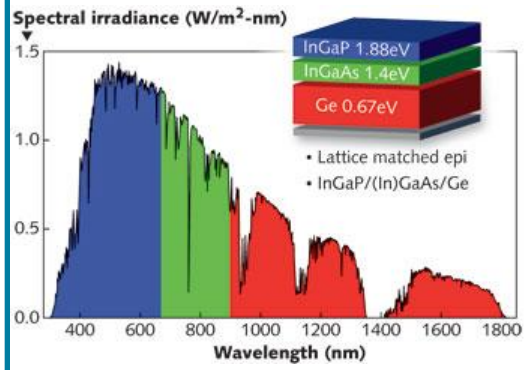
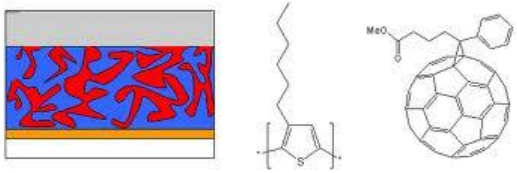
www.laserfocusworld.com



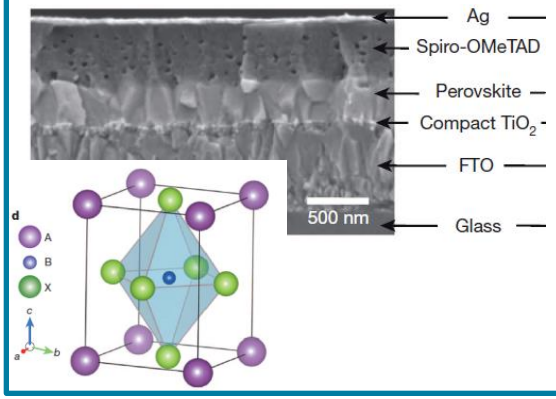
Organic – 11 %

http://www.light.t.u-tokyo.ac.jp

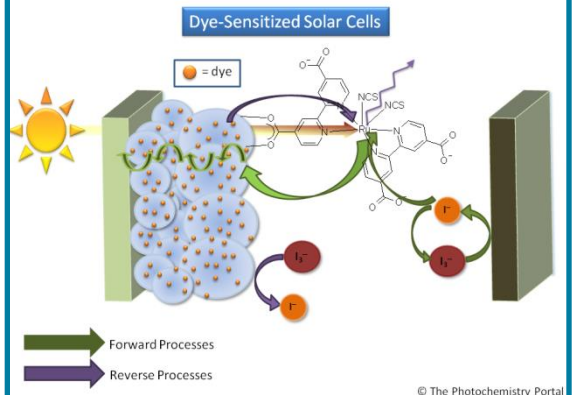


Perovskite – 20.1 %

Liu, Johnston and Snaith
doi:10.1038/nature12509



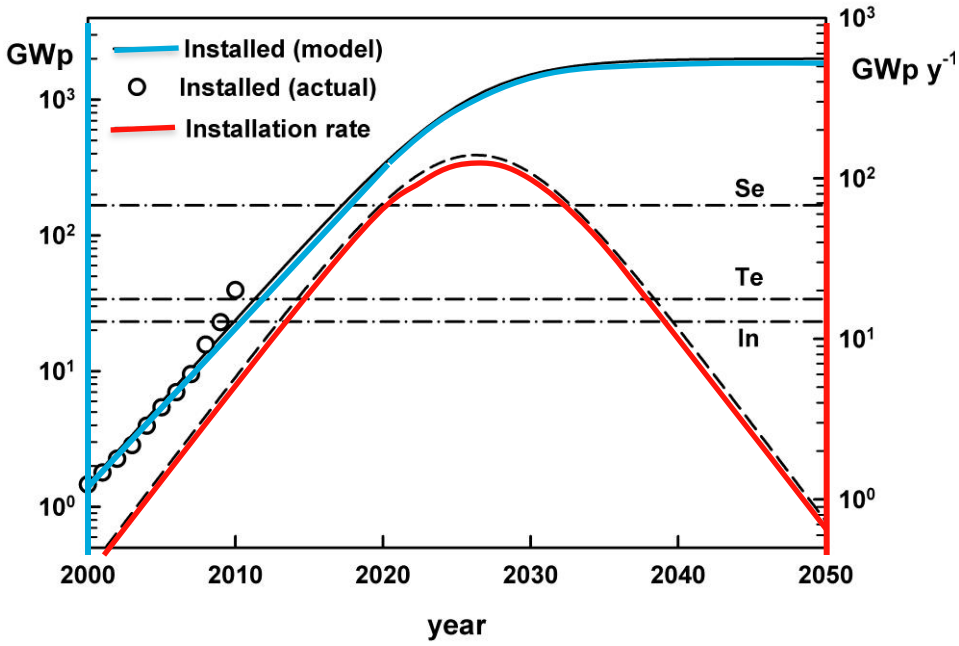
Dye sensitized – 12 %



- Efficient, > 15 %
- Scalable, km^2
- simple & quick to produce, $$$$
- robust, > 20 yrs lifetime

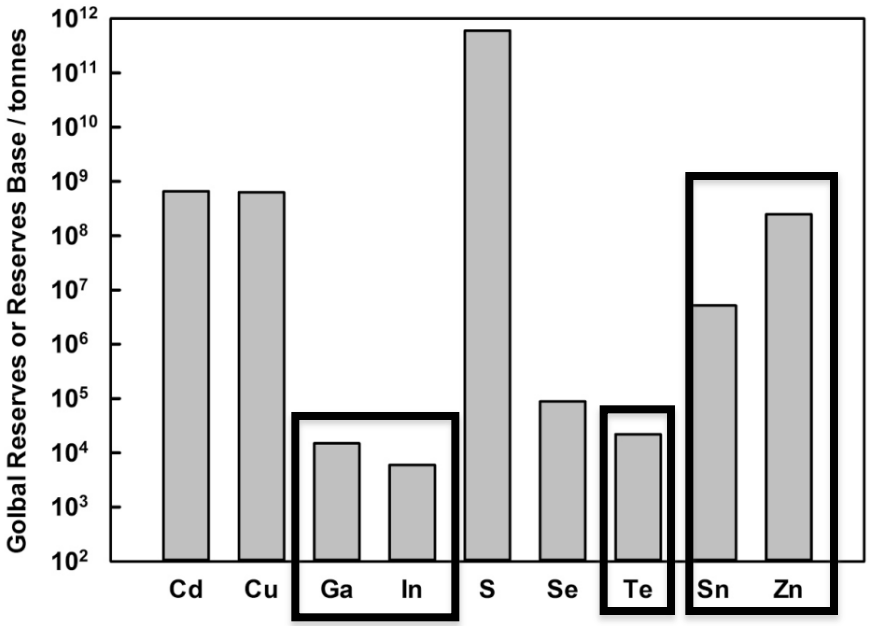
The need for Earth Abundant Thin Film Photovoltaics

[1]



2 TWp would be a few percent of the world power demand

[1]

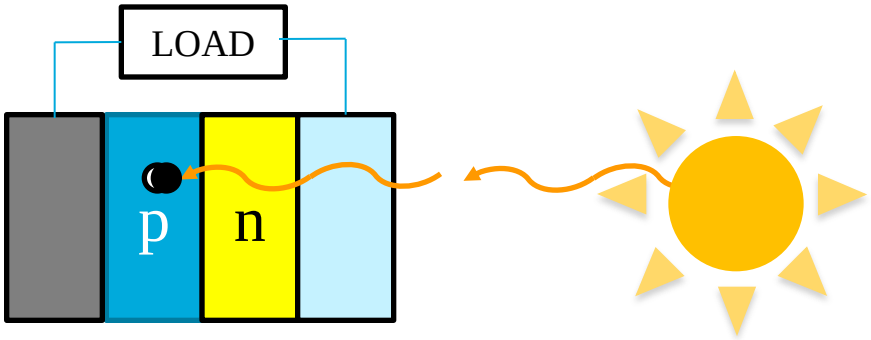


Sn, Zn are more abundant than Ga and In

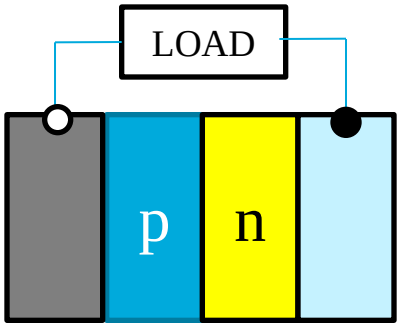
Neither $Cu(In,Ga)Se_2$ nor CdTe is abundant enough for terrawatt deployment

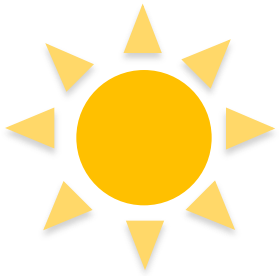
[1] Materials for Photovoltaics, Ian Forbes and Laurence M Peter pp 558-591. In Materials for a Sustainable Future. Eds TM Letcher and JL Scott. 2012. RSC. ISBN 978-1-84973-407-3

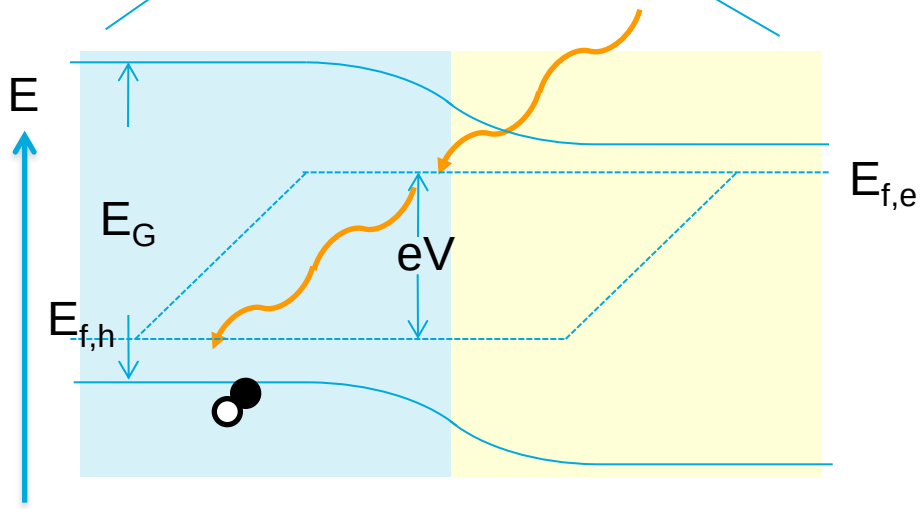
How do Photovoltaic Devices Work?

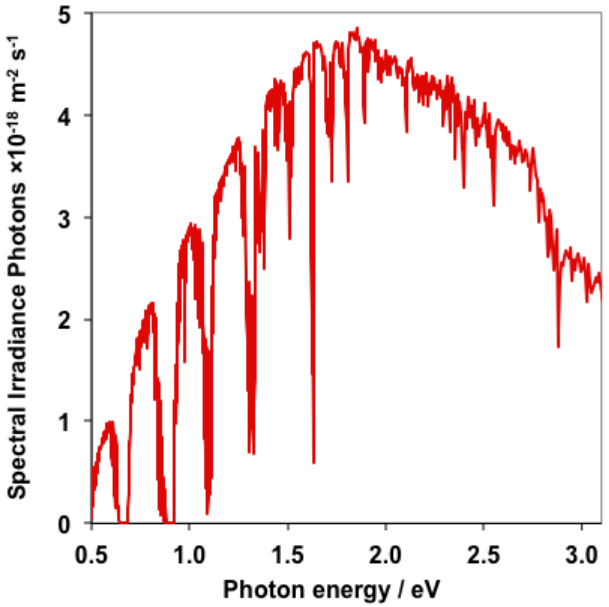


How do Photovoltaic Devices Work?

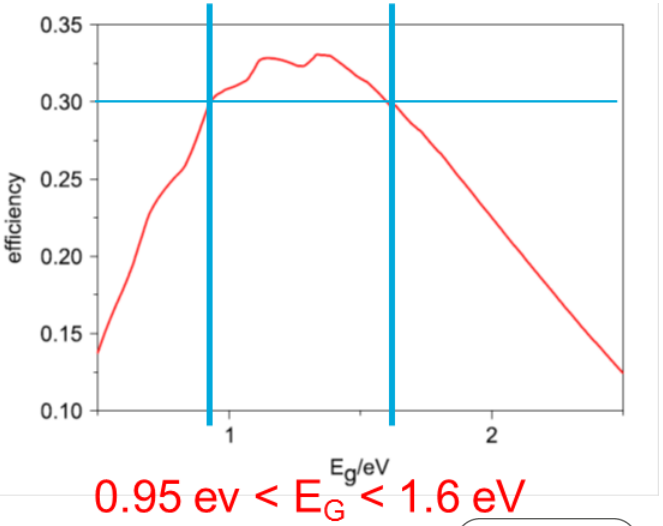








[1]



[2]

Current is the number of electrons extracted
Voltage is the difference in quasi fermi levels

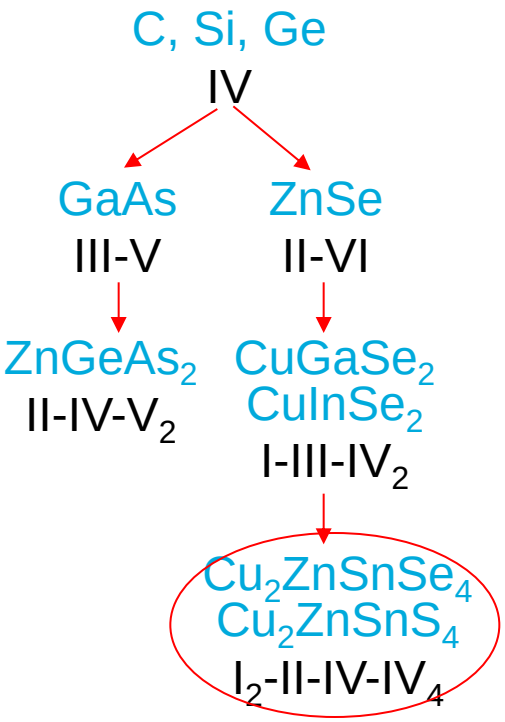
0.95 ev < E_G < 1.6 eV

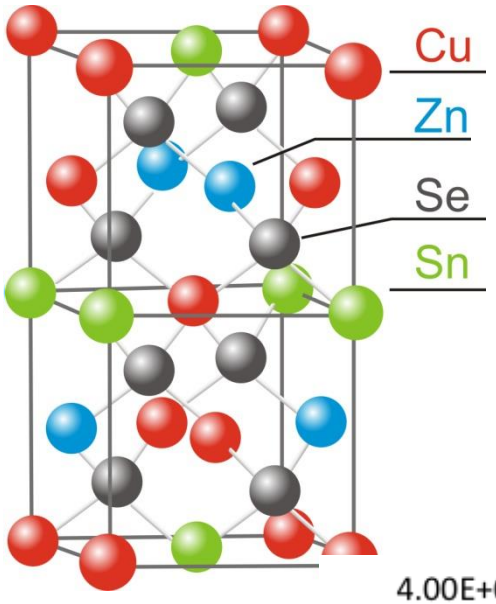
Power output = Current (absorption co-efficient) x Voltage (band gap)

[1] NREL website
[2] Siebentritt, Solar Energy Materials and Solar cells (2011) 95, 6 Pg: 1471

Properties of $Cu_2ZnSn(S,Se)_4$ CZTS

[1]





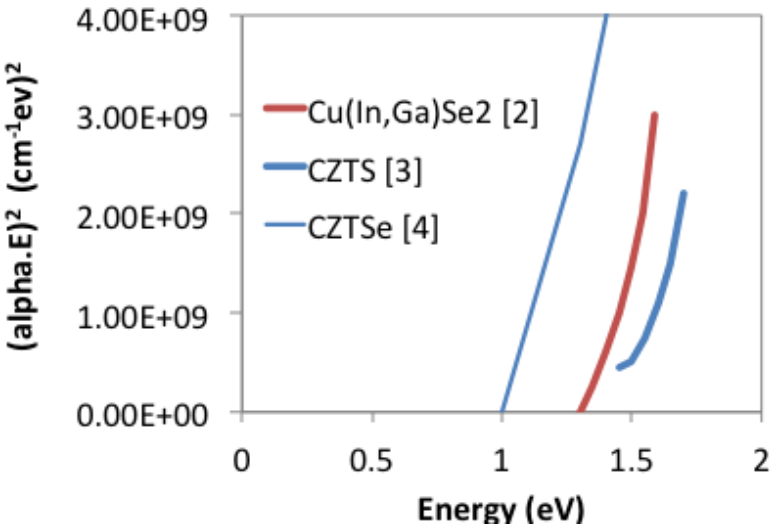
Ia	IIa	III	IV	V	VI
		B	C	N	O
		Al	Si	P	S
Cu	Zn	Ga	Ge	As	Se
Ag	Cd	In	Sn	Sb	Te
Au	Hg	Tl	Pb	Bi	Po
...	...				

Grimm-Sommerfeld-Rule:

4 valence electrons/atom

→ „diamond structure“

Grimm, Sommerfeld
Zeitschrift f. Physik 36, 36 (1926)

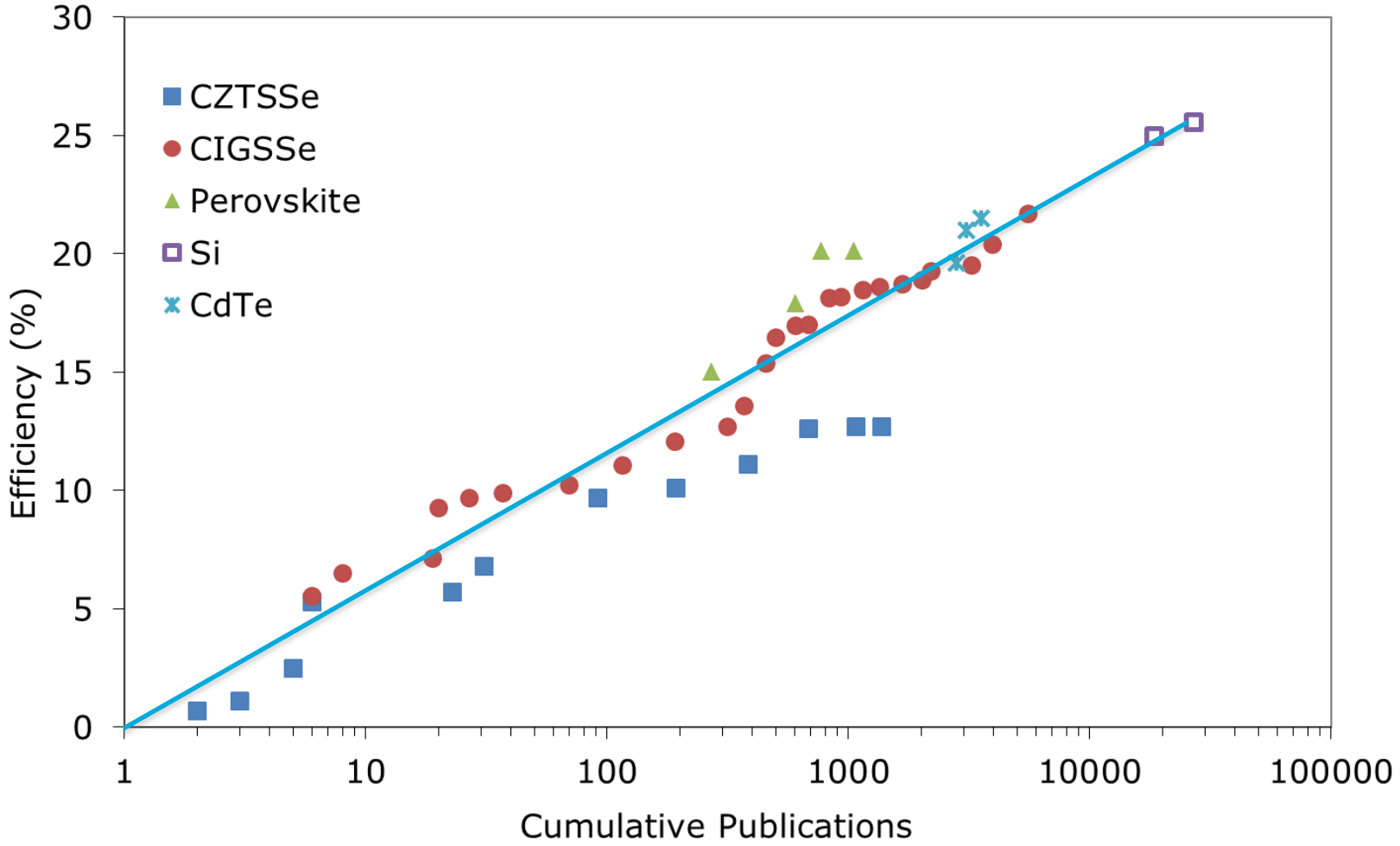


[2,3,4]

Kesterite is a suitable replacement for CIGSe and is earth abundant

[1] courtesy of Susanne Siebentritt, ,[2] Boyle et al. Journal of Applied Physics **115**, 223504 (2014)
[3] Bruc et al. 27th EUPVSEC pg 2763-2766 [4] Guetay et al. APL . 100, 102113 (2012)

Efficiency vs Cumulative Publications from first device

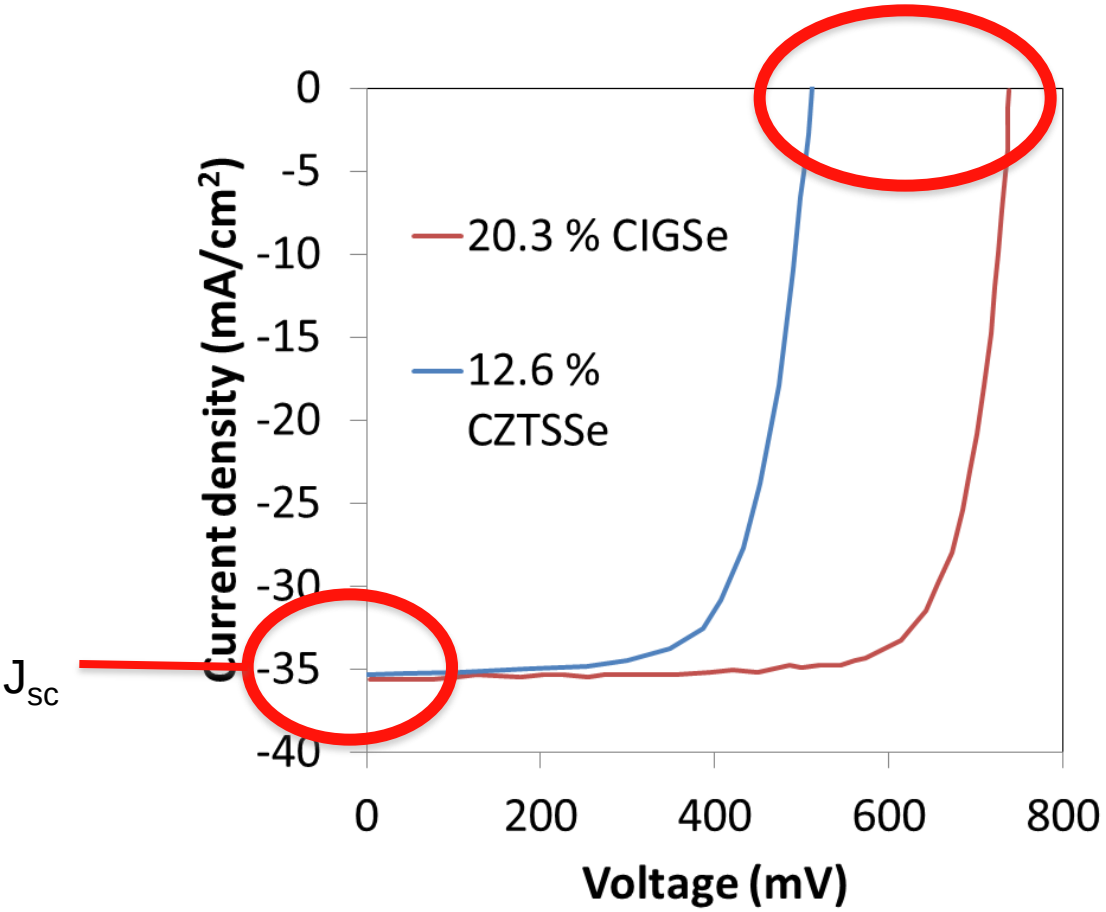


Kesterite efficiency is below the learning curve – why?

What is limiting device performance?

[1,2] E_G = 1.13 eV

V_{oc}



J_{sc}

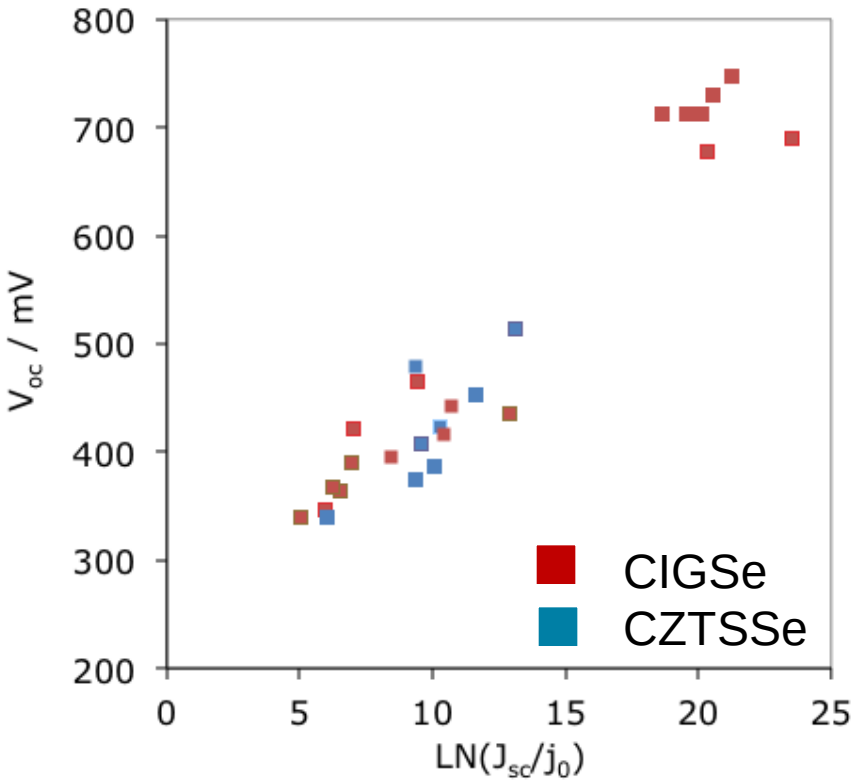
$$J = J_0 \exp\left[\frac{qV}{Ak_BT} - 1\right] - J_{sc}$$

V_{oc} is limiting the device performance – why?

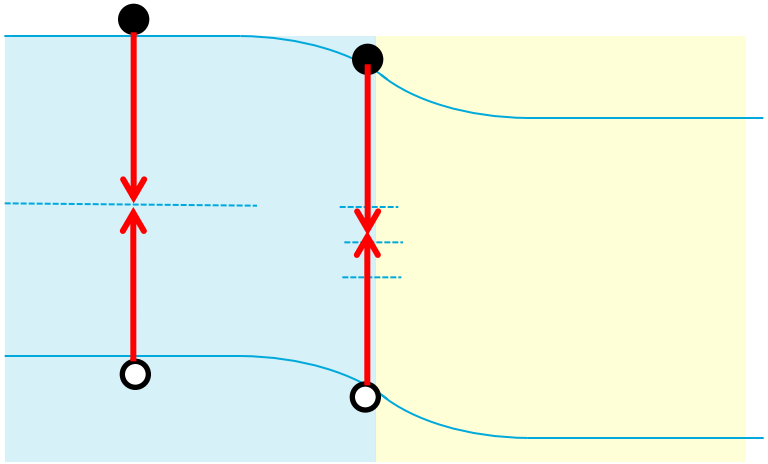
[1] Jackson et al. Prog. Photovolt: Res. Appl. (2011) DOI: 10.1002/pip.1078
[2] Wang et al. Adv. Energy Materials, DOI: 10.1002/aenm.201301465

(1) What is limiting kesterite V_{oc}?

[1a,b]



$$V_{oc} \approx \frac{Ak_BT}{q} \ln\left(\frac{J_{sc}}{J_0}\right)$$



J_0 is the reverse saturation current

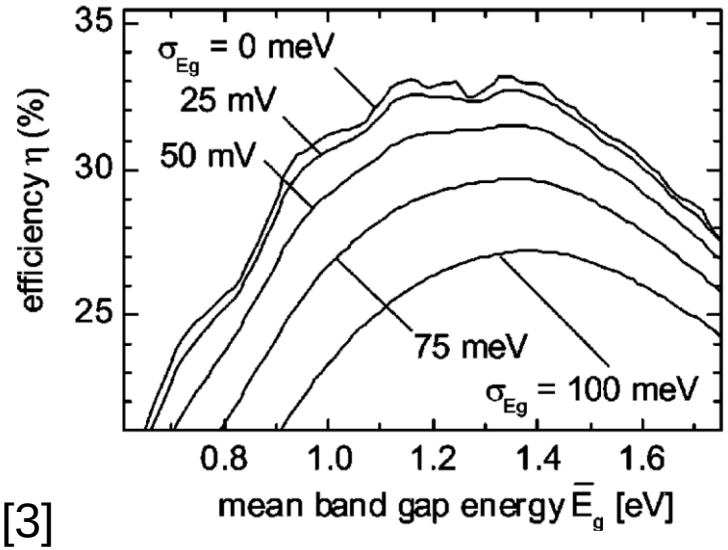
All devices E_G 1 – 1.2 eV

V_{oc} is limited by recombination at defects and surfaces ?

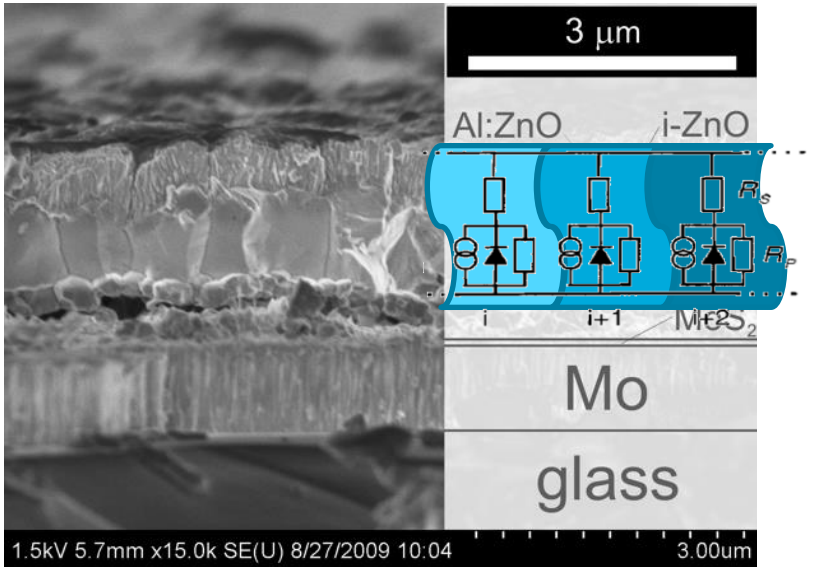
[1] (a) Unpublished data from Yasuhiro Aida, Alex Crossay, Valérie Depredurand, Susanne Siebentritt, Stefan Haass from EMPA, and IREC are gratefully acknolwedged. (b) Literature references

(2) What is limiting kesterite V_{oc}?

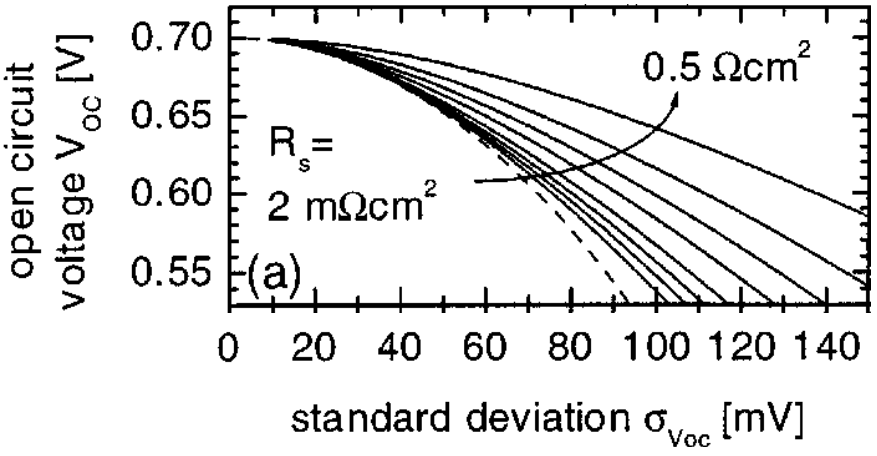
[1]



[2]



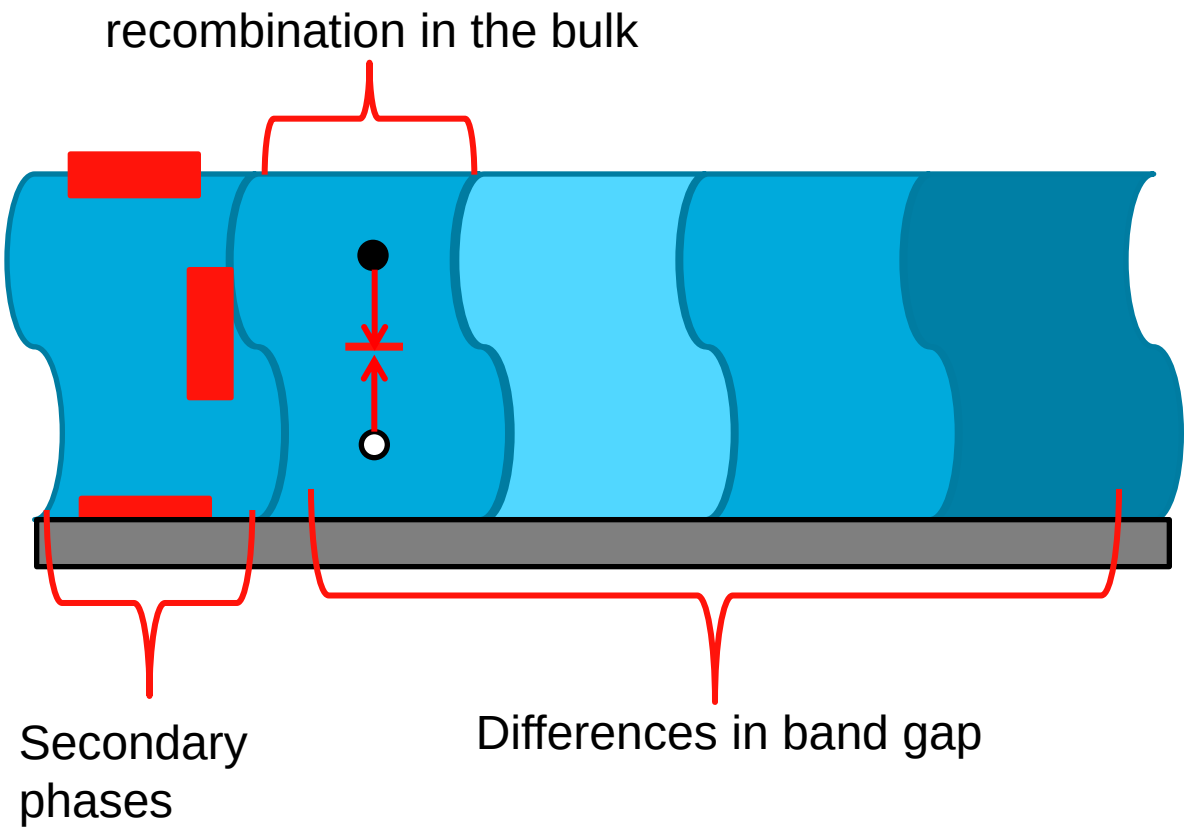
[3]



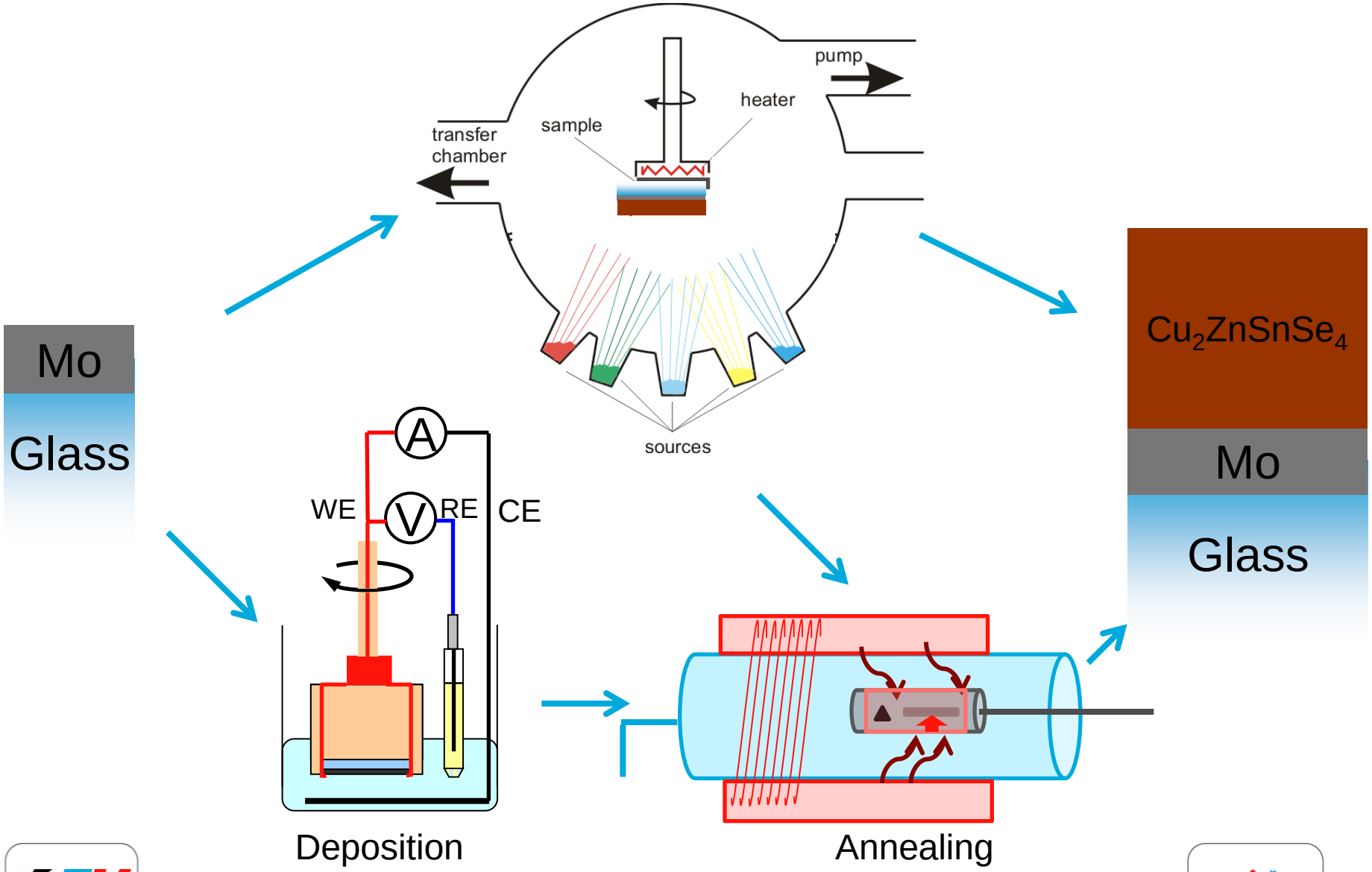
V_{oc} is limited by multiple band gaps?

[1] Rau, Werner, Appl. Phys. Lett 84, 3735 (2004);
[2] Scragg, Berg, Dale, Jnl Electroanalytical Chemistry (2008)
[2] Rau, Grabitz, Werner. Appl. Phys. Lett. 85, 6010 (2004);

Composition and homogeneity are the key?

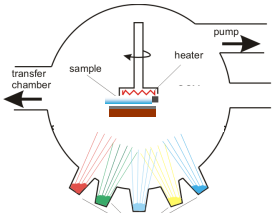


Absorber layer fabrication

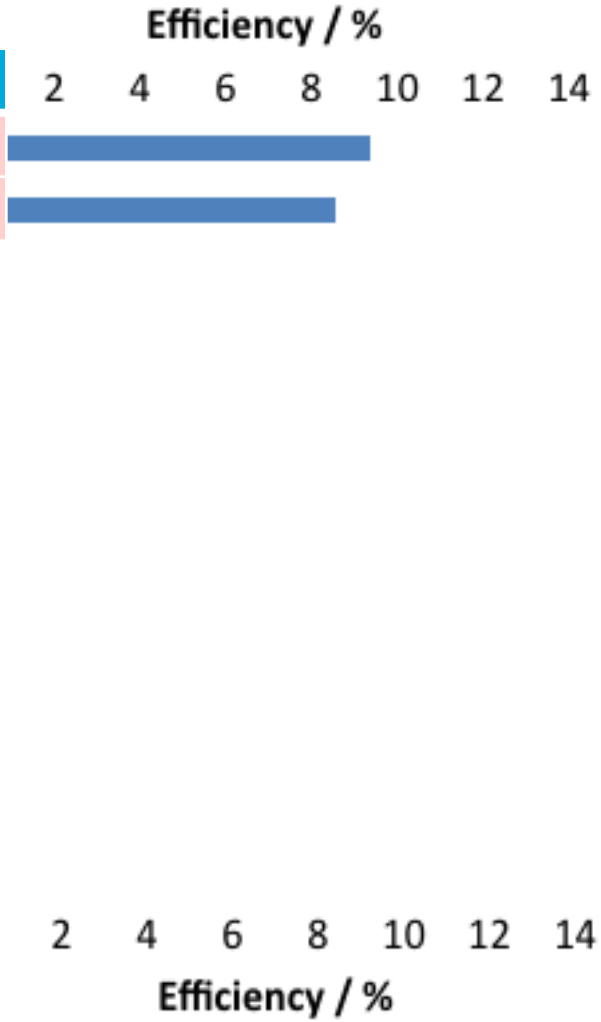


What makes the highest quality absorber? One step or two?

Methodologies pursued



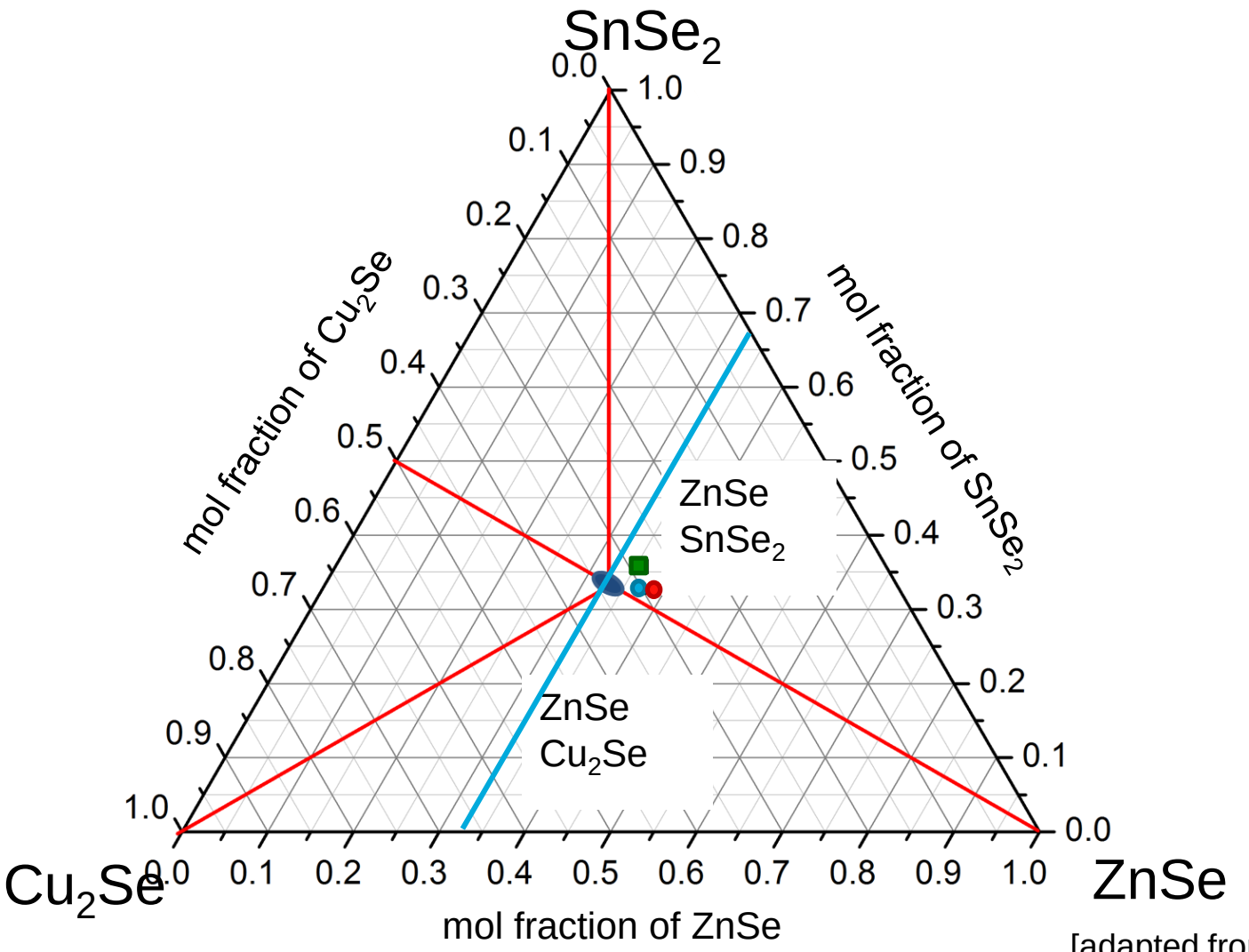
Precursor	Kesterite in	Method
Metals + Chalcogen	1 step	co-evaporation
		monograin



Best process is two stage – all elements intimately mixed in precursor, no carbon residue

[1] Contains unpublished data from IREC and EMPA, IMRA – this conference

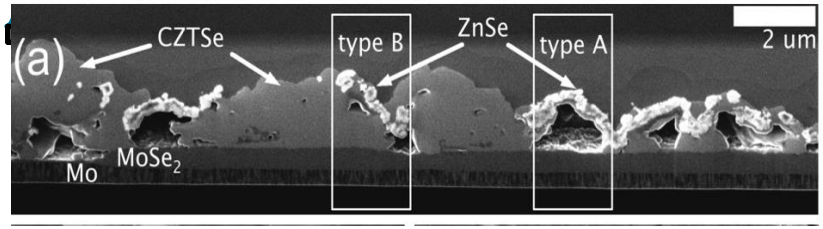
Best devices are not in the single phase region



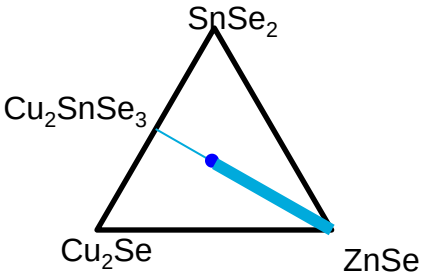
[adapted from 4]

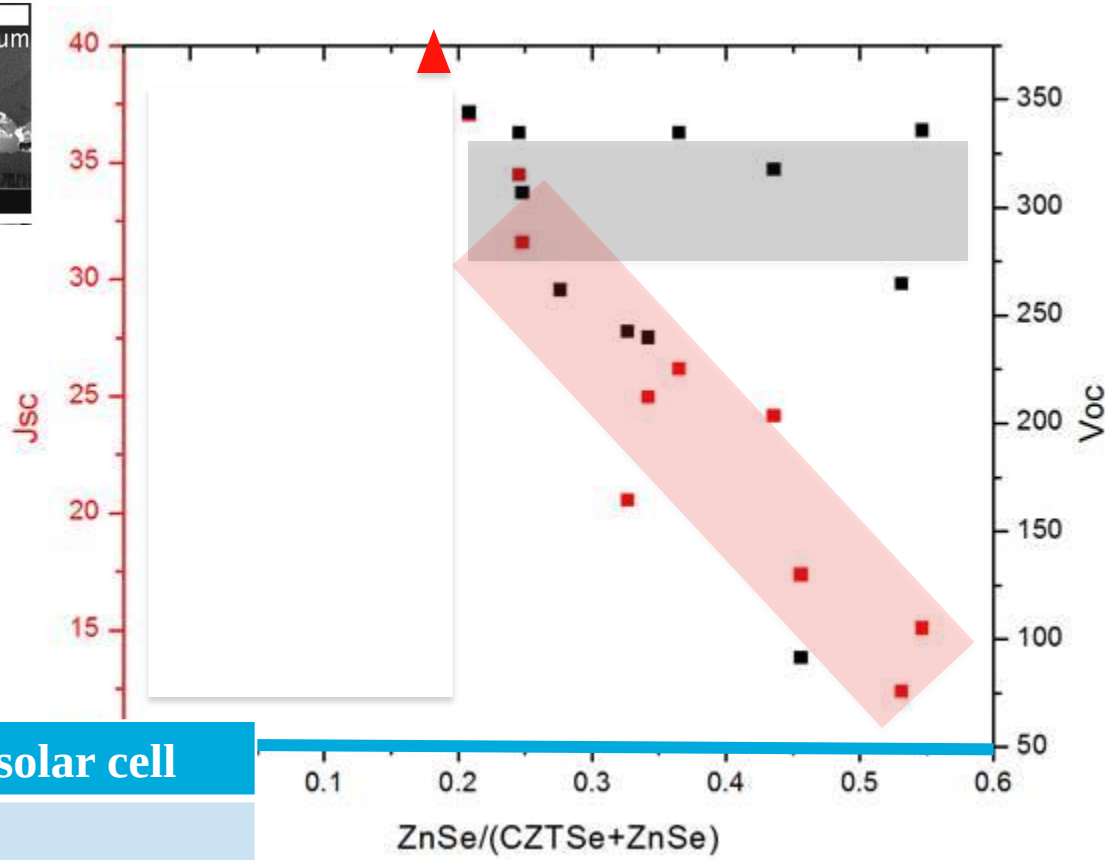
[1] T. K. Todorov *et al.*, *Advanced Energy Materials* **3**, 34 (2013)
[2] I. Repins *et al.*, *Solar Energy Materials and Solar Cells* **101**, 154 (2012)
[3] D. A. R. Barkhouse, *et al.*, *Progress in Photovoltaics* **20**, 6 (Jan, 2012)
[4] I. V. Dudchak, L. V. Piskach, *Journal of Alloys and Compounds* **351**, 145 (2003)

ZnSe secondary phase



[1]





Lee et al. 11.6% IBM
Advanced Energy Materials

[2]

Phase	Band gap (eV)	Effect on solar cell
$Cu_{2-x}Se$	semi-metallic	shunting
ZnSe	2.7	reduces current
SnSe	0.95	reduces voltage
Cu_2SnSe_3	0.5 [3]	reduces voltage

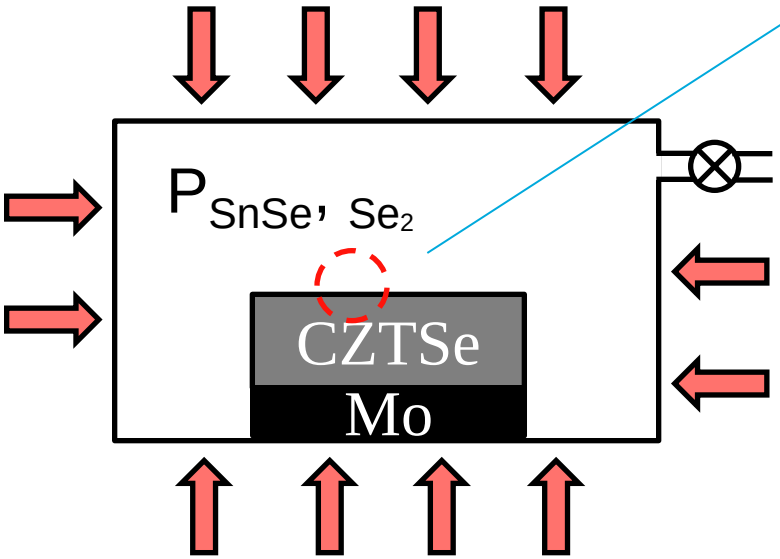
Secondary phases can reduces short circuit current, and voltage

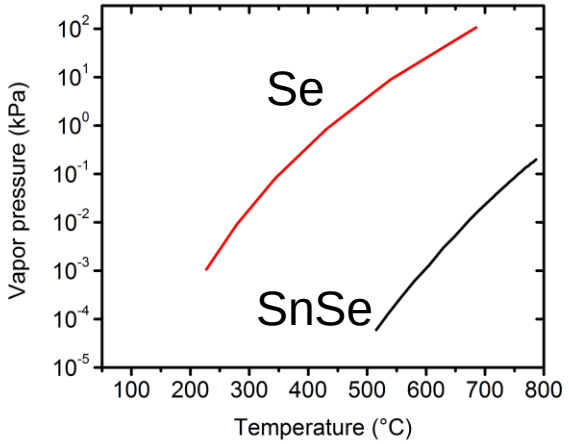
[1] Colombara, Dale et al. Solar Energy Materials & SolarCells123(2014)220–227
[2] Colombara, Dale et al. Advanced concepts in PV (Chapter 5) Royal Society of Chemistry (2014)
[3] Choi et al. APL 1**06**, 043902 (2015)

Secondary phase formation due to CZTSe instability with gas phase

$$Cu_2ZnSnSe_{4(s)} \rightleftarrows Cu_2Se_{(s)} + ZnSe_{(s)} + SnSe_{(s)} + 0.5Se_{2(g)}$$

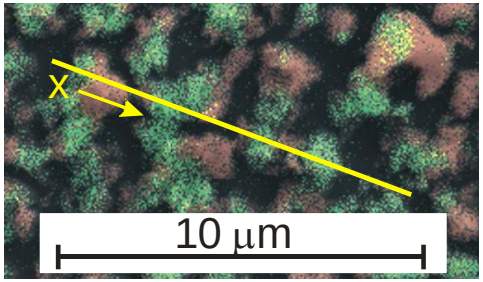
[1,2]





[adapted from 3]

Cu = red
Zn = green
Sn = blue

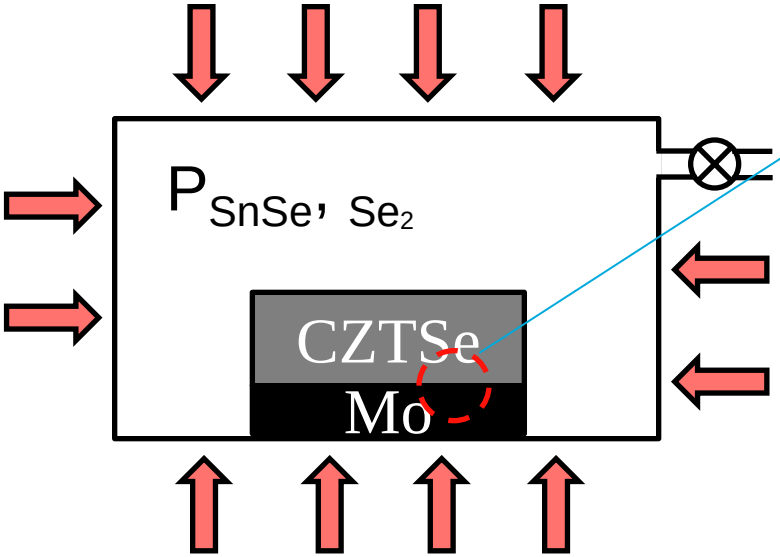


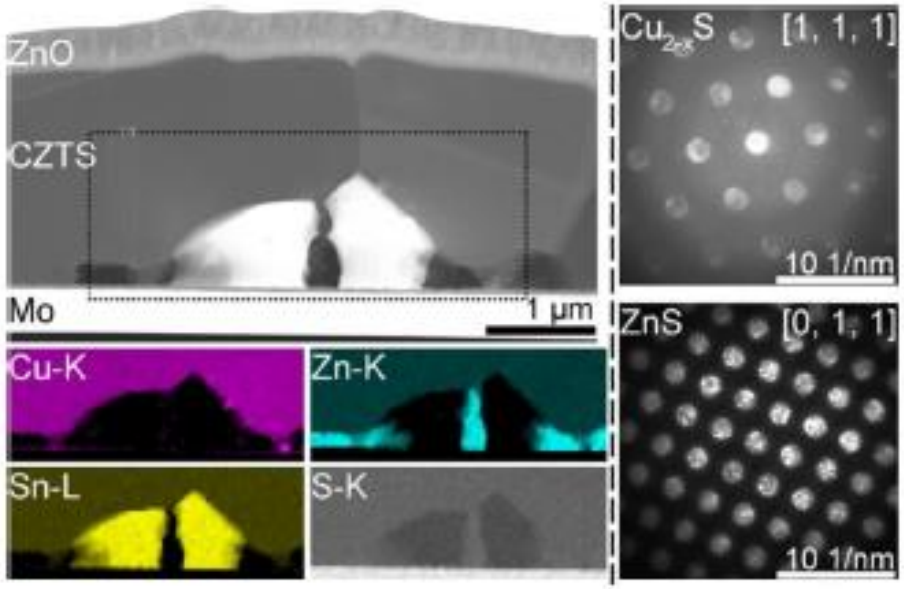
[1]

[1a] A. Redinger, D. M. Berg, P. J. Dale, S. Siebentritt, *JACS* **133**, 3320 (2011)
[1b] D.M. Berg and P.J.Dale Chapter 5 in "CZTS solar cells" Wiley, 2014 ed. K. Ito
[2] A. Redinger *et al.*, *Photovoltaics, IEEE Journal of* **1**, 200 (2011)
[3] F. Zocchi, V. Piacente, *Journal of Materials Science Letters* **14**, 235 (1995)

Secondary phase formation due to CZTSe instability with substrate

$$2Cu_2ZnSnSe_4 + Mo \rightarrow 2Cu_2Se + 2ZnSe + 2SnSe + MoSe_2 \quad [1]$$



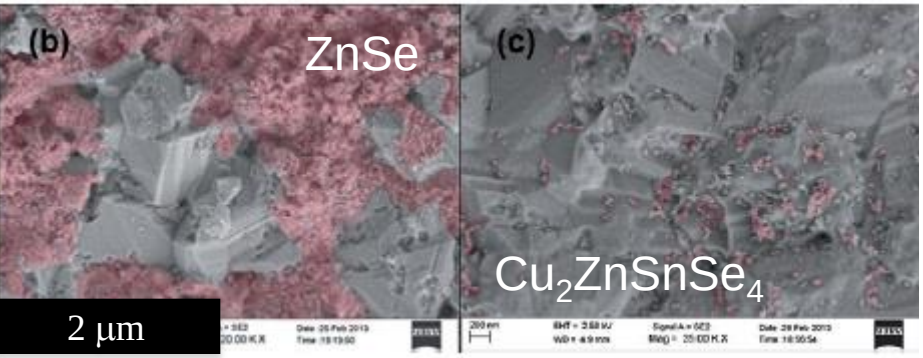


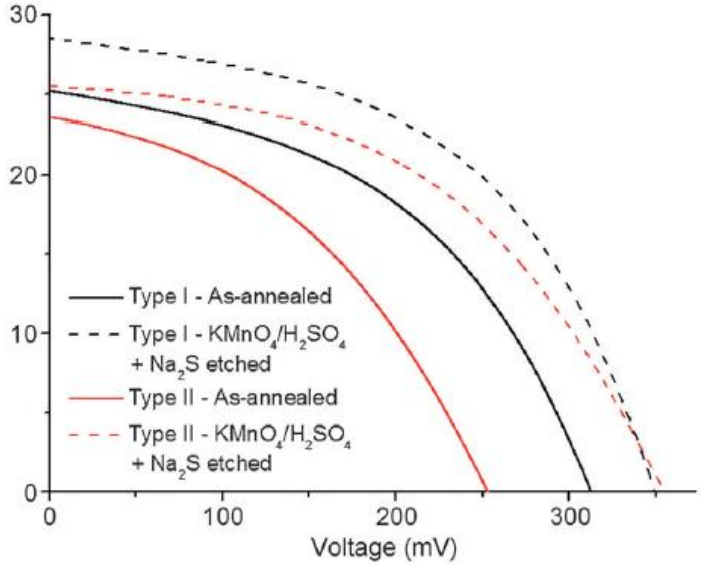
[2]

[1] J. J. Scragg, P. J. Dale, D. Colombara, L. M. Peter, *Chemphyschem* **13**, 3035 (2012)
[2] J. J. Scragg *et al.*, *Journal of the American Chemical Society* **134**, 19330 (2012)

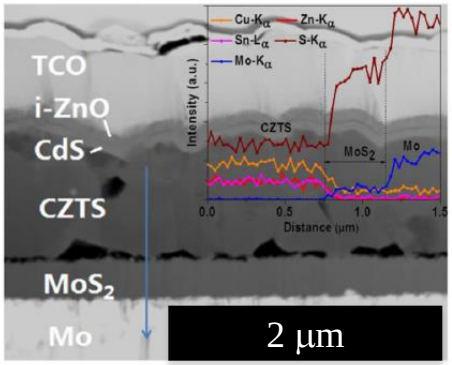
How to deal with secondary phases?

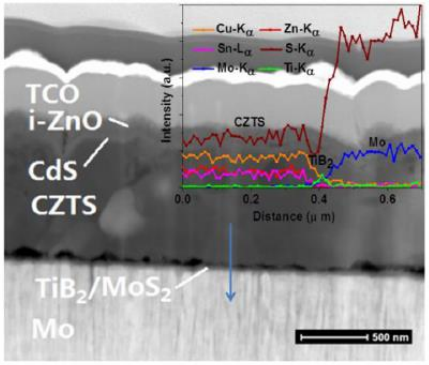
[1] Top surface – chemical etching



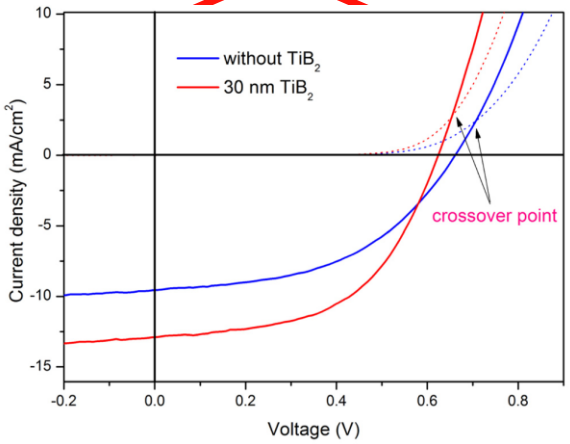


[2] Mo interface – selenium barrier layer





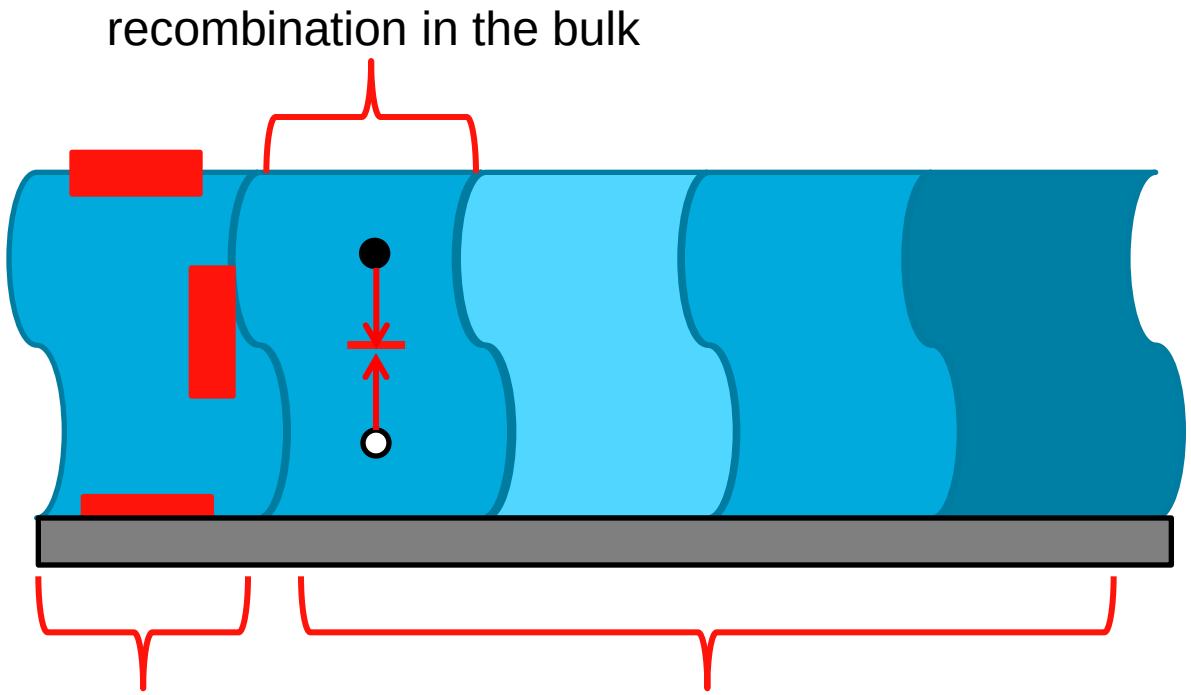
$2Cu_2ZnSnSe_4 + Mo \rightarrow 2Cu_2Se + 2ZnSe + 2SnSe + MoSe_2$

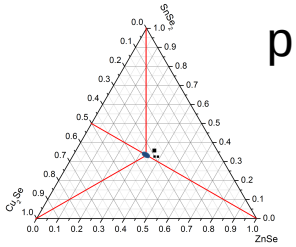


Chemical etching removes secondary phases, barrier layers reduce formation

[1] Lopez-Marino et al. Chem. Eur. J. (2013), 19, 14814 – 14822
[2] Liu et al. Applied Physics Letters 104, 051105 (2014)

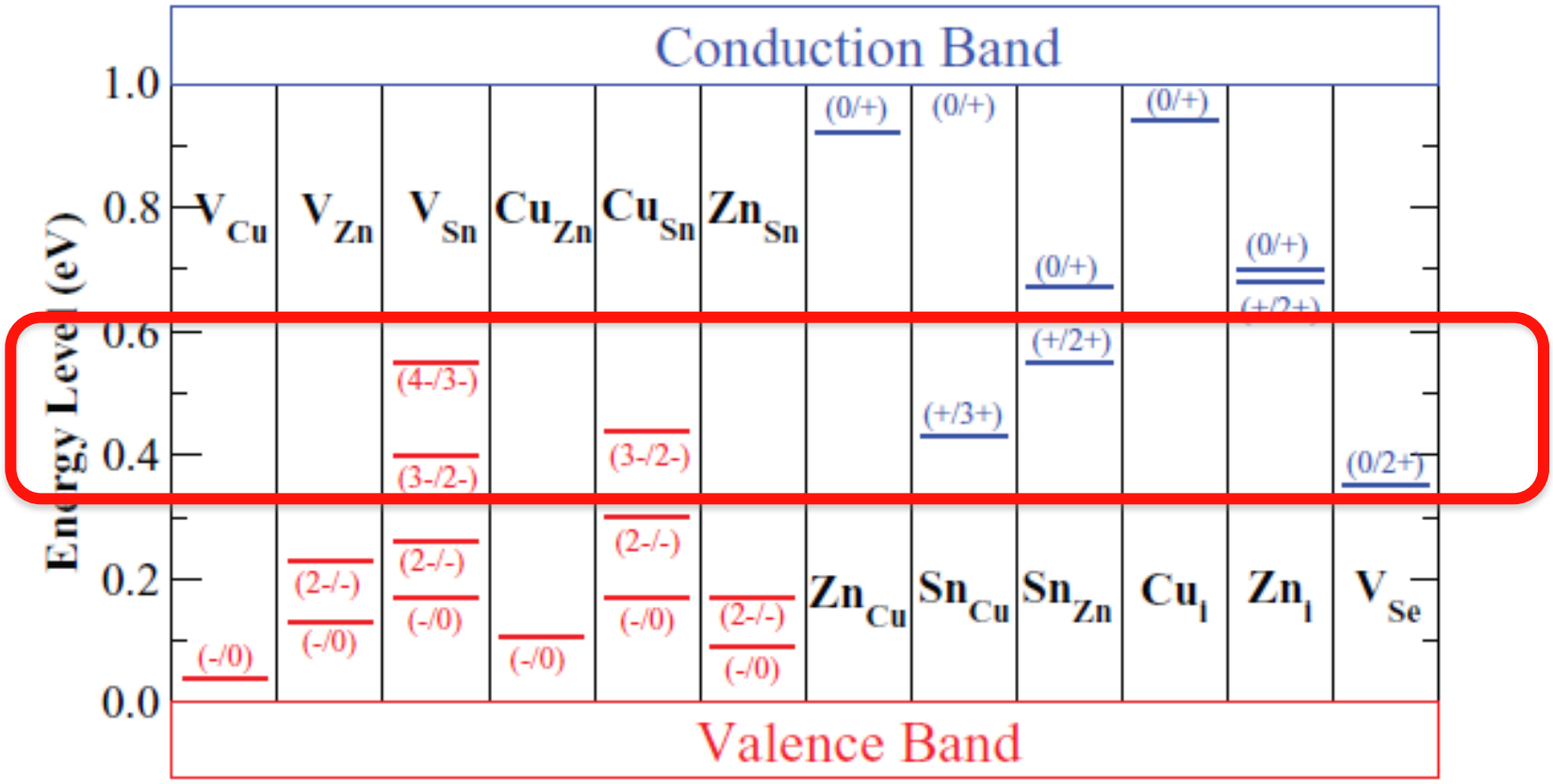
Composition and homogeneity are the key?





$$Cu_2ZnSnSe_{4(s)} \rightleftarrows Cu_2Se_{(s)} + ZnSe_{(s)} + SnSe_{(s)} + 0.5Se_{2(g)}$$

Defect states in the bulk

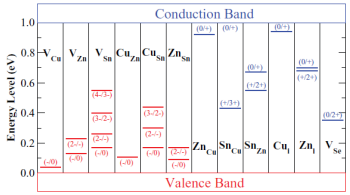


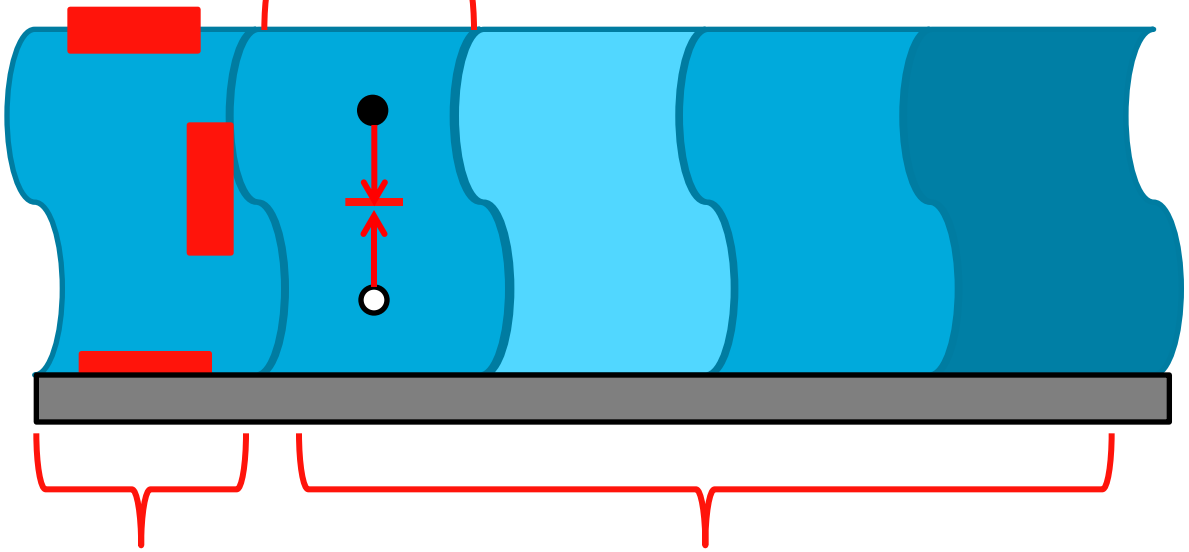
Sn heavily implicated for deep defects and thus high recombination

Chen et al. *Adv. Mater.* **2013**, *25*, 1522–1539

Composition and homogeneity are the key?

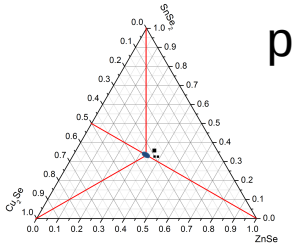
recombination in the bulk





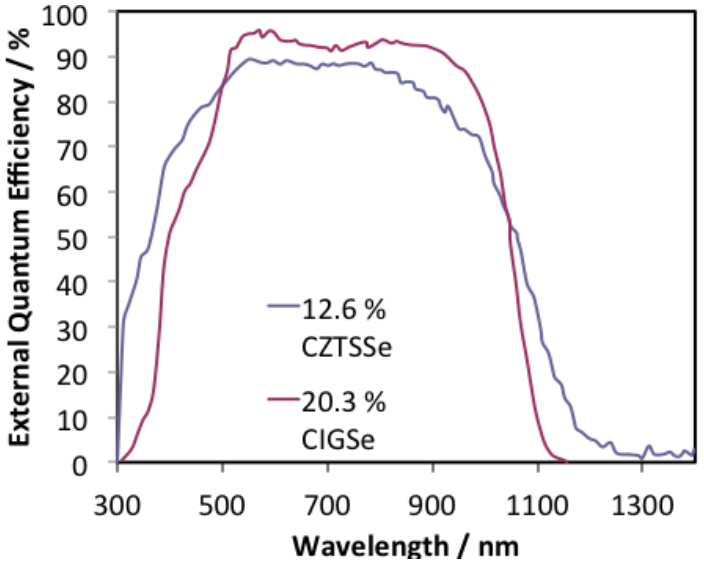
Secondary phases

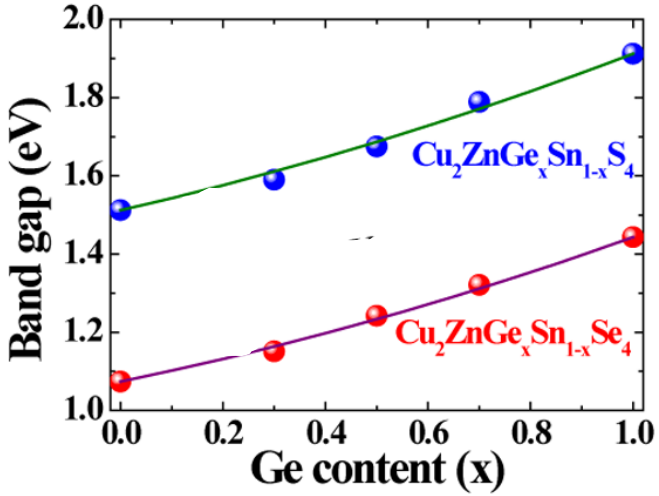
Differences in band gap



$$Cu_2ZnSnSe_{4(s)} \rightleftarrows Cu_2Se_{(s)} + ZnSe_{(s)} + SnSe_{(s)} + 0.5Se_{2(g)}$$

Voc deficit problem due to mixed band gaps

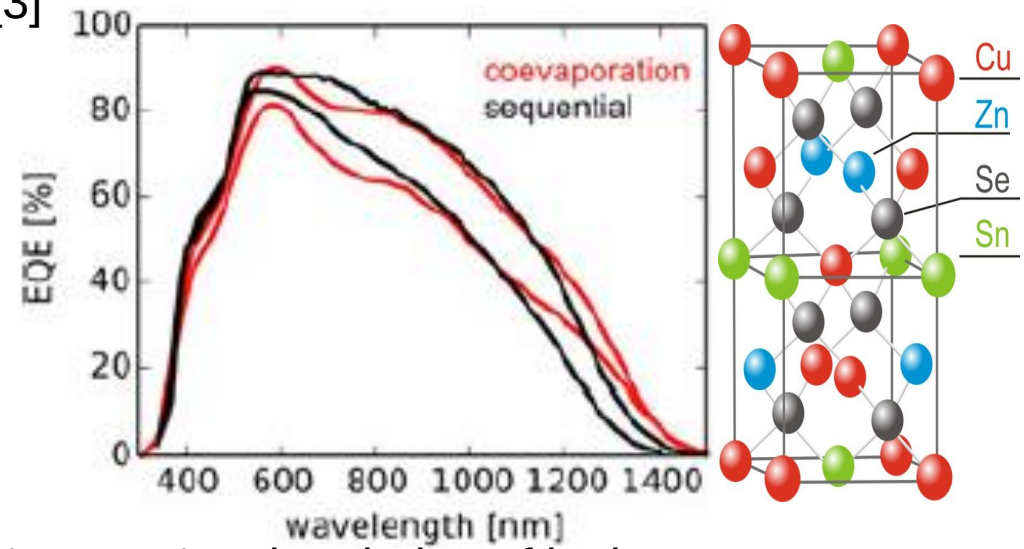


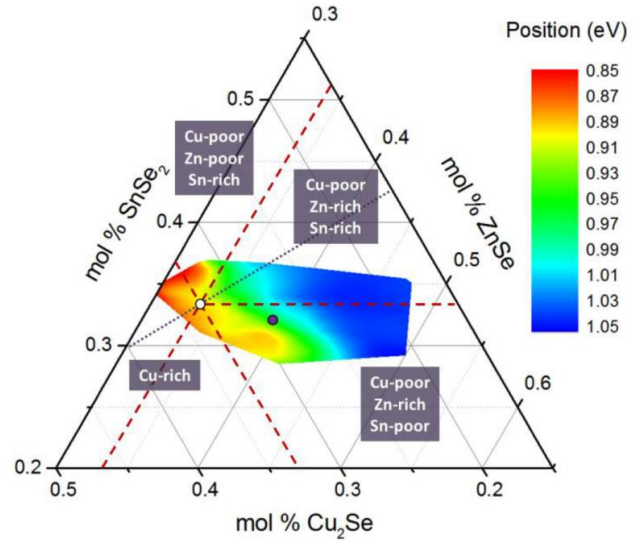


[1]

Chemical substitution

[3]





[2]

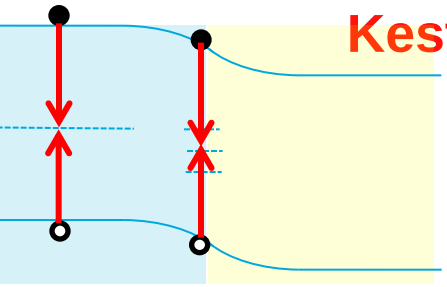
Disordering of lattice

Chemical defects

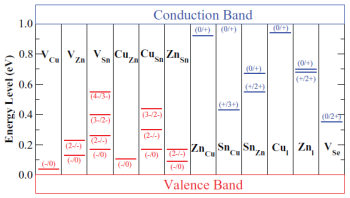
Three possible reasons for multiple band gaps at least!

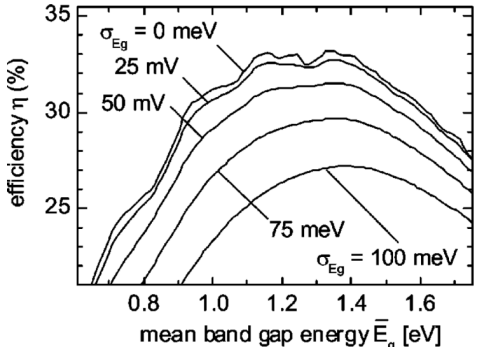
[1] Khadka and Kim, J. Phys. Chem. C 2015, 119, 1706−1713 [2] Collord, Xin, Hillhouse, IEEE Jnl of PV 5, 1 (2015)
[3] Redinger, Dale et al. IEEE Jnl of PV 5, 2 (2015)

Kesterite Summary on voltage loss mechanisms

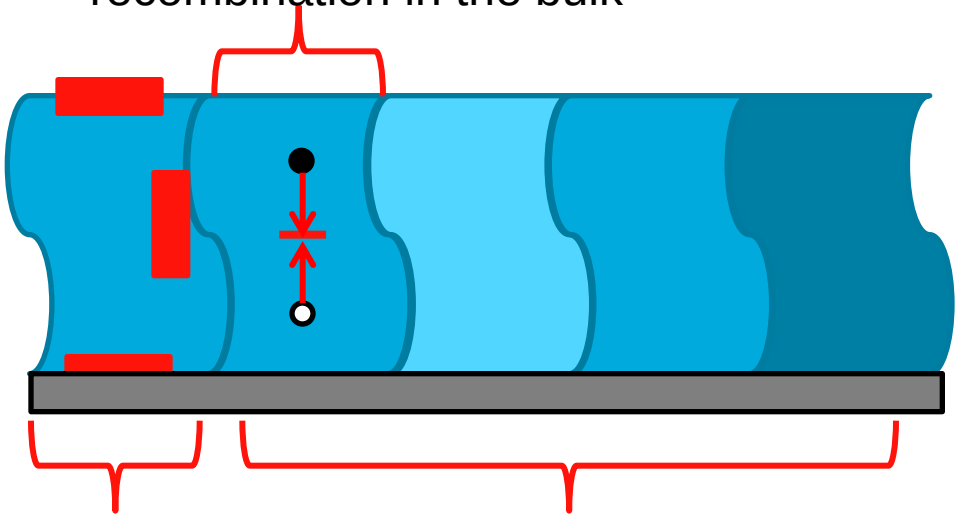


J_0 is the reverse saturation current



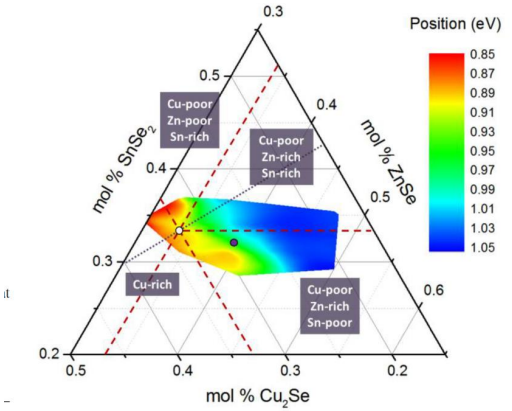


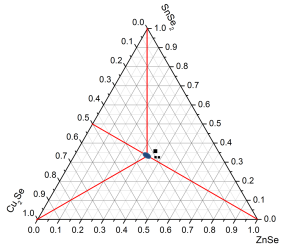
recombination in the bulk

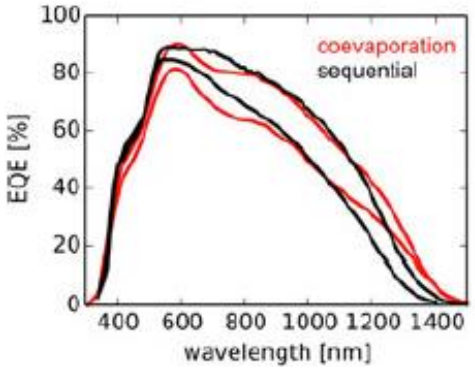


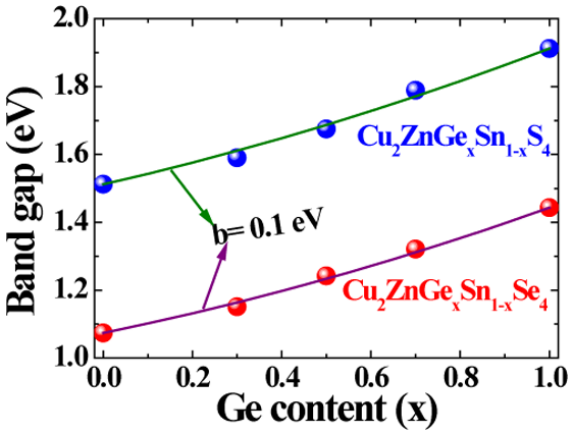
Secondary phases

Differences in band gap



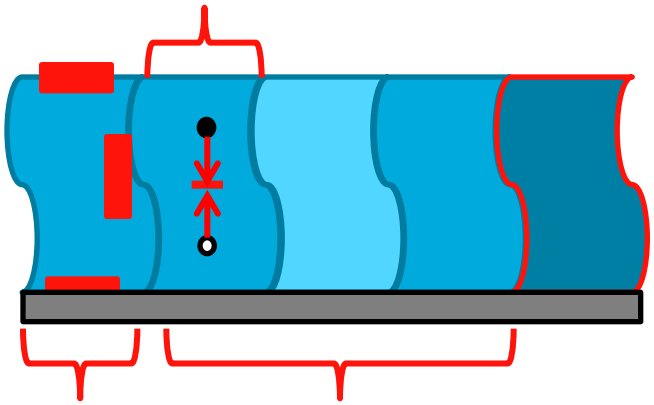






$Cu_2ZnSnSe_{4(s)} \rightleftarrows Cu_2Se_{(s)} + ZnSe_{(s)} + SnSe_{(s)} + 0.5Se_{2(g)}$

Time to panic? Not yet



role of grain boundaries and alkali dopants

- Uniform precursor deposition essential on a sub-micron scale
- Back contact is thermodynamically inert and provide ohmic contact
- Annealing atmosphere is controlled to avoid changes in composition
- Secondary phases only nucleate on the surface to be etched away
- Band gap grading is implemented like in $Cu(In,Ga)Se_2$
- Buffer and window layer optimization (more transparent in the IR)